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# PMR study of intra-molecular motions in solid protocatechualdehyde

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Proton magnetic resonance study of polycrystalline protocatechualdehyde ($C_7H_6O_3$) has been made in the temperature range from 77°K to 427°K (melting point). Upto the room temperature the molecular motions remain frozen. Above the room temperature the analysis of experimental data show the rotation of OH groups about their respective C–O bonds and near melting point that of CHO group. The molecular structure has also been confirmed.

## 1. INTRODUCTION

Proton magnetic resonance experiment has been performed on polycrystalline protocatechualdehyde (3.4 dihydroxy benzaldehyde) to study the molecular motions inside the crystal lattice at various temperatures and to verify the molecular structure. The change in the resonance line shape with rise in temperature has been taken as a measure to find out these molecular reorientations : 3, 4 dihydroxy benzaldehyde has been taken for study due to its importance in chemical and biochemical fields.

In the absence of any precise data regarding the molecular structure of protocatechualdehyde, the molecular model of the compound has been taken up assuming the standard values of the bond distances and angles. The benzene ring was assumed to be symmetrical with bond distances C–C = 1.37Å and C–H = 1.09Å. The C–C bond connecting the aldehyde group was assumed to be 1.50Å with C–O = 1.201Å, C–H = 1.07Å, $\angle CCH = 124°6'$ and $\angle CCO = 123°2'$. The OH groups were assumed to be in the plane of ring.

## 2. EXPERIMENTAL DETAILS

The NMR experiments were performed at Tata Institute of Fundamental Research (Bombay), using a Varian Associate's variable frequency spectrometer and an associated nuclear induction probe with a 12″ magnet system. The resonance frequency was 7.5 Mc/S. The temperature was varied by regulating the flow of heated or cooled nitrogen gas over the sample with the help of a variable temperature NMR probe accessory. The accuracy of determination of second moment is about ±1.0 gauss[2]. Sample of high purity 3, 4-dihydroxy benzaldehyde was obtained from C.D.R.I., Lucknow.

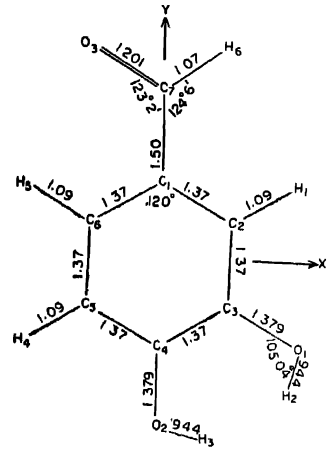


Fig. 1. Molecular model of 3, 4 dihydroxy benzaldehyde.

## 2. Calculation and Results

The experimental values of the second moment at different temperatures were calculated from the NMR derivative tracings of the line shape derivatives $g(H)$ by means of the expression

$$S = 1/3[\int_0 g(H)(H-H_0)^3 dH \Big\backslash \int_0 g(H)(H-H_0)dH] \quad \ldots (1)$$

where $H_0$ is the resonance field value

Eq. (1) can be simplified to the expression

$$S = \frac{\Sigma h^3 f(h)}{3\Sigma h f(h)} \text{ gauss}^2 \quad \ldots (2)$$

by applying the trapezium rule to the integrals (Pake *et al* 1948) where $h = H-H_0$ and $f(h)$ is a function of $h$ in arbitrary units and contains different number of terms at different temperatures depending upon the line shape

The graph showing the variation of second moment with temperature is shown in figure 2. The value of second moment at 77°K was found to be 13.58 gauss$^2$.